

THE PREPARATION METHOD OF OUTSIDE-IN POLY VINYLIDENE FLUORIDE  
HOLLOW FIBER MEMBRANE SPINNED UTILIZING A IMMERSION-COAGULATION  
METHOD AND THE PRODUCT THEREOF

**BACKGROUND OF THE INVENTION**

[0001] 1. Field of the Invention

[0002] The present invention relates to a method of producing hollow fiber membranes, in particular, the present invention relates to a method of producing an outside-in polyvinylidene fluoride hollow fiber membranes that are spun utilizing an immersion-coagulation process and a formulation for polymer solution which produces the membrane thereof, comprising high molecular weight polyvinylidene fluoride resin and high proportional organic additives, and relates to a hollow fiber membranes produced by the method and the polymer solution as well.

[0003] 2. Background of the invention

[0004] Polyvinylidene fluoride resins (PVDF) have been regarded as one of the most important materials for membrane separation technology, which have excellent separating properties and chemical stability.

[0005] Production of separation membranes from PVDF resins using a spun immersion-coagulation process (or namely immersion-precipitation process) are well known in the prior art. Polymeric membranes may be prepared by phase inversion technique which commences with the formation of a molecularly homogeneous, single phase solution of a polymer in a solvent. The solution is then allowed to undergo transition into a heterogeneous, metastable mixture of two interspersed liquid phases one of which subsequently forms a gel. Phase inversion can be achieved by solvent evaporation, non-solvent precipitation and thermal precipitation. In the case of immersion-coagulation process (or namely immersion-precipitation process), phase inversion is achieved by precipitation of non-solvent in accordance with polymer, so that polymeric membrane is prepared. In the field, the process can also be called NIPS (non-solvent induced phase separation), and the most known non-solvent of PVDF resin includes water and alcohols such as ethanol, with water being particularly preferred because it is the most inexpensive non-solvent and can be used in large amount. For example, US patent No. 4,399,035 discloses that any non-solvent of polyvinylidene fluoride type resin may be used as the coagulating liquid, and that water is particularly preferred because it is the most inexpensive

non-solvent and can be used in large amount.

[0006] In conventional processes, polyvinylidene fluoride resins (PVDF) used in accordance with the membrane formation generally have an average molecular weight (Mw) ranging from 30,000 to 200,000, which ensures that the prepared hollow fiber membrane will have more strength by increasing the weight percent of the PVDF resins in the solution. For example, U.S. Patent No. 5,066,401 discloses membranes which were based on a homogeneous mixture of polyvinylidene fluoride resins. The solution contained 70 to 98 percent by weight of polyvinylidene fluoride. However, increased concentration of the PVDF resins consequentially resulted in high melting temperature (the melting temperature for the solution of the above mentioned membrane is up to be more than 240°C). This has a disadvantage of untimely secondary effect of thermally induced phase separation, which will certainly influence the structure of the prepared membrane. On the other hand, such hollow fiber membrane prepared by the method has desirable strength in some measure, but the porosity is unfortunately low. Especially while the polymer melted with higher temperature, more gas and cavity is discharged which results in higher density of the solution and lower porosity and large pore size (the average pore size of the above mentioned prepared membrane is 0.45 $\mu$ m).

[0007] However, PVDF is one kind of hydrophobic resin, so it tends to form hydrophobic dense skins while formation. Furthermore, lower molecular weight PVDF resins usually means larger pore size, and higher molecular weight PVDF resins usually means smaller pore size of the prepared membrane. Many PVDF membranes are reported, such as flat porous membranes, hollow fiber inside-out membranes, etc., most of these membranes have nominal pore size in the range of 0.1 $\mu$ m -0.45 $\mu$ m, and the structure of cross-sectional supporting layer mostly includes bidirectional macroporous of finger-structure and needle-structure, directional macroporous of finger-structure, or partial macroporous of finger-structure, and the like, throughout the cross-section of the membranes.

[0008] Asymmetrical membranes usually comprise porous supporting layers and thin skins, and there will be observed macroporous finger-structures and needle-structures throughout the supporting layer result from liquid-liquid phase separation (shown in Fig.6 and Fig.7). However, the macroporous structure will obviously be disadvantageous for the prepared membrane, as there will be weak parts in the prepared membrane and which will be even easy to be deposition while filtration application.

[0009] Though porous PVDF hollow fiber membranes prepared by conventional process have skin layers, the macropores of their supporting layers will damage the mechanical strength (as an example of Japanese patent of JP 1-22003B).

[0010] In order to improve process technique, an application for a method of PVDF hollow fiber

porous membrane was filed for a Chinese patent (App. No. 95117497.5) which discloses a method of forming PVDF hollow fiber membranes with macropores having high permeability and asymmetrical structure, via wet-dry process, of which the polymer solution included the following substances: polyvinylidene fluoride 15-25 wt%, nonsolvent 0.5 -5 wt%, surfactant 1-10 wt%, high molecular pore-forming agent 1-20 wt% and solvent 40-82.5 wt%.

[0011] And a further Chinese patent application ( No.98103153.6) was filed for a method of PVDF hollow fiber porous membranes and the products thereof, which discloses a method for preparing PVDF hollow fibre porous membranes via a dry-wet method, in which the prepared membrane was stretched with the stretch ratio controlled at 60-300%. The porous membrane had 0.1-1 $\mu$ m of nominal pore size, 300-1000 L/ m<sup>2</sup>.h (0.1 MPa) of purified water throughput and 70-90% of porosity.

[0012] All of these known hollow fiber membranes have the disadvantage that the compressive strength will easily be influenced during applications, and contamination will easily be deposited on the surface of the membranes, and the membrane performance will attenuation. Furthermore, due to surface tension of the water, the ultrafiltration membrane manufactured by conventional techniques which mostly have such micropore that the water flux is lower, and limits their application in the field of water treatment.

## **SUMMARY OF THE INVENTION**

[0013] The present invention solves the problem of conventional techniques which causes the proportion of lower molecular weight PVDF resins to be unsuitable for preparing polymer solution, the preparing process to be too complicated, and is also to solve the problem of conventional techniques in which water permeability of the prepared membrane is not high enough, and the problems of undesirable mechanical properties, undesirable permeability stability and short service life, due to macroporous finger-structure supporting layer of the prepared membranes for higher water flux.

[0014] It is an object of the present invention to provide a polymer solution formulation which produces the membranes thereof, comprising high molecular weight polyvinylidene fluoride resin and high proportional organic additives (as pore-forming agent), and a method of producing an outside-in PVDF hollow fiber membrane spun utilizing immersion-coagulation process.

[0015] It is another object of the present invention to provide a microporous outside-in PVDF hollow fiber ultrafiltration membrane, which has asymmetrical structure with opposite inner and outer skins, and has porous supporting layer of sponge-structure network, and the said porous

supporting layer is not macroporous throughout the cross-section.

[0016] According to the present invention, a method to prepare a microporous outside-in PVDF hollow fiber membranes which are spun by immersion and coagulation, comprises:

a. preparing polymer solution by introducing the following material into a mixer, dissolving and stirring it the mixture at a certain temperature:

Polyvinylidene Fluoride	18-25%(wt);
Organic additives	22-25%(wt);
Inorganic additives	0.5-5.0%(wt);
Solvent	59.5-45.0%(wt).

b. extruding the resulting solution through an outer tube of a double tube spinneret, and lumen forming composition liquid through inner tube of the same simultaneously;

c. obtaining original fiber membrane by introducing and immersing the extruded polymer solution as well as the lumen liquid into a first stage coagulation bath, and consequently into a second coagulation bath after quick evaporation, wherein a precipitation takes place via phase inversion in the said two baths respectively;

d. passing the original fiber membrane through a rinsing bath, subjecting it to hydrophilic rendering;

then an outside-in hollow fiber with double skins and complete spongy network is prepared.

[0017] As polyvinylidene fluoride resins from which the microporous hollow fiber membrane of the present invention is prepared, there are high molecular weight vinylidene fluoride homopolymers, which are useful to ensure the desired mechanical properties of the prepared membrane, and to avoid the problem such as bad melting flowability and moldability due to high concentration of PVDF resin. On the other hand, the use of such polyvinylidene fluoride resins combined with higher proportional organic additives (which acts as pore-forming agent) has solved the problem which will affect the properties of the prepared membrane, and created a good condition for preparing the said membrane according to the present invention.

[0018] According to the present invention the weight molecular weight (Mw) of the polyvinylidene fluoride resins ranges from 400,000 to 800,000 daltons, and a characteristic viscosity of the polyvinylidene fluoride resins ranges from 1.65-2.00 (102 ml/g. 30°C).

[0019] Preferably, the molecular weight (Mw) ranges from 500,000 to 700,000 daltons, and a characteristic viscosity ranges from 1.75-1.85 (102 ml/g. 30°C). If there is more than one kind of PVDF resins, the total amount shall be constant.

[0020] According to the present invention, while the polymer solution is prepared, and is extruded through a double tube spinneret, after quick evaporation (preferably 0.02-0.2 seconds), subsequently the resulting extrudate is immersed in at least a coagulating bath where a exchange

between the coagulating liquid and the solvent happens simultaneously on the both surfaces of outside and inside of the original fiber. The exchange on the both surfaces interact each other and will consequently influence the final structure of the prepared fiber.

[0021] As is well-known in the case of using non-solvent as coagulation liquid, during the first coagulation period, there generally have too high exchange rate between the coagulating liquid and solvent, this would either cause the formation of a large pore size and macroporous supporting layer structure of the prepared membrane, or cause incomplete exchange and thus lower porosity, because, while the solvent is continuously exchanged from the solution, the component of the coagulation continuously is changed, and the exchange rate becomes less and less, and consequently decreases the coagulating effect.

[0022] For these reasons, it is helpful to control exchange rate between the solvent and the coagulation liquid, in order to decrease the precipitation velocity on the two skins of the original membrane, which are the inner and outer skins, via a two stage coagulation process. Furthermore, for the same purpose, it is helpful to add a certain content of solvent for the PVDF resin to coagulation liquid which comprises a non-solvent for said PVDF resin, so as to decrease the concentrate difference of the solvent between the coagulation liquid and the original membrane and control diffusion and exchange dynamic forces.

[0023] According to the present invention, the method immersing the resulting extrudate into a two stage coagulating bath, so as to control the solvent exchange rate of the outside skin of the original fiber, for a time of 1.5s to 4.0s in the first bath containing 40-80% by weight of solvent, and then into the second bath containing 5-30% by weight of solvent for 4s to 120s, for the purpose of delaying phase separation. It is very important to ensure that the exchange rate of the inside skin (the lumen forming liquid) is faster than that of the outside one.

[0024] According to the present invention, the lumen forming composition liquid consists of 10-80% by weight of solvent of PVDF resins, 5-30% by weight of alcohol and polyalcohol, 0.5-5% by weight of surfactant, and deionized water.

[0025] According to the present invention, the method also includes controlling the solvent exchange rate of the inside skin, decreasing the precipitation velocity so as to avoid macropore and neckdown phenomenons that can result from the viscosity of the lumen liquid while under traction.

[0026] According to the present invention, a microporous outside-in PVDF hollow fiber ultrafiltration membrane is prepared with partial cross-section of gradually increscent sponge network that is porous from outside skin to inside (as shown in Figs.1-5). This solves the problem that there are macropore in the structure of the hollow fiber prepared by conventional technology.

[0027] According to the present invention, the kinds and concentration of additives are also key factors for the property of the prepared fiber. For various polymer solution systems, there are large differences of influence with same additives. For example, the more molecular weight of an additive such as polyvinylpyrrolidone (PVP) etc. always influences macropore, which can change molecular crosslinking degree of the solution, while less molecular weight additive such as lithium chloride etc. influences micropore. The additive with less molecular weight can enter the voids between the molecule chain of the polymer and is introduced to the functional groups, which improve the stability of the prepared fiber. Generally, suitable ratios of various additives will be helpful to obtain desirable pore diameter pattern and improved flux of the prepared fiber.

[0028] According to the present invention, besides the above mentioned factors which affect the properties of the prepared fiber, the pore-forming agent also influences the pore diameter pattern. Partially the agent acts as filler of the voids among the polymer solution. During the coagulation process of the extruded fiber, the pore-forming agent will be extracted, and while the agent and solvent diffuse and exchange, thereby voids are formed throughout the fiber. To obtain fiber with desirable porosity and pore diameter, it is important to control the concentration of the pore-forming agent and diffusion velocity of the same.

[0029] According to the present invention, a high desirable concentration of organic additives is used to decrease the melting temperature of the PVDF polymer. This is conducted to prepare homogenous polymer solution. Furthermore the organic additives also act as pore-forming agents. Preferably, the said organic additive consists of at least two of the groups of polyvinylpyrrolidone, polyethylene glycol, polyvinyl alcohol, Tween and Triton. If the additives are more than two kinds, the total amount is constant.

[0030] According to the present invention, the polymer solution comprises 22-25% by weight of the said organic additive. Preferably, the organic additive is polyvinylpyrrolidone having a molecular weight ranging from 11,000 to 1,000,000 daltons.

[0031] According to the present invention, the inorganic additive is selected one or two from the group comprising lithium chloride, lithium nitrate and sodium acetate solution. If the additives are more than two kinds, the total amount is constant.

[0032] According to the present invention, the solvent is selected one or two from the group comprising N-Methyl Pyrrolidone, dimethylformamide, dimethyl acetamide, dimethyl sulfoxide and triethyl phosphate. If the solvent is more than two kinds, the total amount is constant. The results of the solvent show formation of the original skins which are helpful to improve exchange rate of the solvent.

[0033] According to the present invention, the lumen forming liquid is a mixture comprising 10-80% by weight of solvent of PVDF, 5-30% by weight of alcohol and polyalcohol, 0.5-5% by

weight of surfactant and a balance of deionized water.

[0034] According to the present invention, the evaporating time before phase separation is preferably ranges from 0.02s to 0.2s; the first stage coagulating bath preferably comprises 40-80% by weight of solvent of PVDF resin in which the time of coagulation is 1.5s to 4.0s; and the second stage bath preferably comprises 40-80% by weight of solvent of PVDF resin in which the time of coagulation is 4.0s to 120s.

[0035] According to the present invention, the hydrophilic agent is selected at least one or more from the group comprising 10-80% by weight of propanetriol, 0.05-5% by weight of hydroxypropyl cellulose and 0.5-5% by weight of Triton.

[0036] According to the above mentioned process, a microporous outside-in PVDF hollow fiber ultrafiltration membrane is prepared that has double skins which are internal and external in which said external skin is denser than said internal skin, and a complete sponge network supporting layer of the cross-section between the internal and external.

[0037] The microporous hollow fiber membrane according to the present invention has an nominal pore diameter ranging from 0.01 $\mu$ m to 0.06 $\mu$ m.

[0038] Furthermore, the microporous hollow fiber membrane according to the present invention has a porosity of 70%-85%, a compressive strength of more than 0.5Mpa, and a pure water flux per unit wall thickness of 150 to 800L/m<sup>2</sup>h (25°C, 1bar).

[0039] As described above, compared to conventional techniques, the method of preparing a microporous hollow fiber membrane of the present invention, including integrated and continuous process of evaporation, immersed spinning, two stage phase separation and coagulation, hydrophilic rendering, is simple and feasible. The resulting membrane has properties of high compressive strength, high flux, high contamination removal ability, and high performance stability. The membranes of the present invention are useful in a variety of application such as biochemical, food, medical, brewing and purifying industry, and domestic applications as well.

## **BRIEF DESCRIPTION OF THE DRAWINGS**

[0040] FIG. 1 is an electron micrograph of a cross-section of a hollow fiber membrane according to the present invention;

[0041] FIG. 2 is an electron micrograph of a part cross-section of a hollow fiber membrane according to the present invention;

[0042] FIG. 3 is an electron micrograph of the external skin of a hollow fiber membrane

according to the present invention;

[0043] FIG.4 is an electron micrograph of the sponge-structure supporting layer of a hollow fiber membrane according to the present invention;

[0044] FIG. 5 is an electron micrograph of a longitudinal section of a hollow fiber membrane according to the present invention;

[0045] FIG.6 is an electron micrograph of a cross section of a conventional hollow fiber membrane;

[0046] FIG.7 is another electron micrograph of a cross section of a conventional hollow fiber membrane.

### **DESCRIPTION OF THE PREFERRED EMBODYMENT**

[0047] The invention is further described by examples and combining with figures as following.

#### **EXAMPLE 1**

[0048] As shown in Table 1, 18% by weight of polyvinylidene fluoride resin (FR904 as trade name available from Shanghai 3F company) having a molecular weight of 800,000 daltons and a characteristic viscosity of 1.95 (102 ml/g. 30°C); 12.5% by weight of polyvinylpyrrolidone having a molecular weight of 45,000 daltons (PVP K-30, K-90 as trade name available from Shanghai Shenpu Co.); 8% by weight of PEG-600 (imported from Japan); 1.5% by weight of Tween-80 (imported from Japan); 0.5% by weight of lithium nitrate; 29.5% by weight of N-Methyl Pyrrolidone (available from Shanghai chemical reagent Co.); and 30% by weight of dimethylacetamide (available from BASF Co.) were added in order and blended together in a mixer. The resultant mixture was melted stirring at 85°C, and continuously degassed so as to be a homogenous dope. The resultant solution was then extruded through a outer tube of a double tube spinneret while holding the temperature of 80°C and co-extruded with the lumen forming liquid through inner tube of the same simultaneously. The lumen forming liquid consists of 50% by weight of solvent of PVDF, 8% by weight of alcohol and polyalcohol, 5% by weight of surfactant and 37% by weight of deionized water (shown in Table 3). The resulting extrudate was evaporated while passing it through the air for a short time of 0.1s, and then passed through the first stage aqueous coagulating bath for 4s, which containing 40% by weight of solvent of PVDF resin, and then passed through the second stage aqueous coagulating bath containing 5% by weight of solvent of PVDF resin for 60s by traction. The hollow fiber-shaped extrudate thus obtained was subsequently subjected to water washing, hydrophilic rendering with which the composition of 50% by weight of propanetriol, 0.1% by weight of hydroxypropyl cellulose and 1.0% by weight of Triton (shown in Table 2) and drying. Finally, the prepared hollow fiber



membrane was taken up on the gathering wheel.

[0049] The prepared hollow fiber membrane, out-to-in, has external skin 1, complete sponge-structure supporting layer 2 and internal skin 3 respectively, in the cross-section as shown in Figs. 1-5.

[0050] The microporous hollow fiber membrane had an outer and inner diameter of 1.25mm, 0.65mm respectively, an average pore diameter of 0.045 $\mu$ m, and a porosity of 75%. The compressive strength of the microporous hollow fiber membrane was 0.5Mpa, and the purity water flux per unit wall thickness was 450L/m<sup>2</sup>h (at 25°C, 1bar).

#### **EXAMPLE 2~10**

[0051] Example 1 was repeated to prepare a microporous hollow fiber membrane except for various blend components and technique parameters used which are listed in Tables 1, 2 and 3, respectively. The properties of the prepared membranes are shown in Table 4.

#### **EXAMPLE 11**

[0052] 18% by weight of polyvinylidene fluoride resin (FR904 as trade name available from Shanghai 3F company) having a molecular weight of 800,000 daltons; 12.0% by weight of polyvinylpyrrolidone having a molecular weight of 45,000 daltons (PVP K-30 as trade name available from Shanghai Shenpu Co.); 0.5% by weight of polyvinylpyrrolidone having a molecular weight of 1,000,000 daltons (available from Nanjing Jinlong Co.); 8% by weight of PEG-600 (imported from Japan); 1.5% by weight of Tween-80 (imported from Japan); 0.5% by weight of lithium nitrate; 29.5% by weight of N-Methyl Pyrrolidone (available from Shanghai chemical reagent Co.); and 30% by weight of dimethylacetamide (available from BASF Co.) were added in order and blended together in a mixer. The resultant mixture was melted while stirring at 85°C, and continuously degassed so as to produce a homogenous dope. The resultant dope was then extruded through outer tube of a double tube spinneret while holding the temperature of 80°C and co-extruded with the lumen forming liquid through inner tube of the same simultaneously. The resulting extrudate was evaporated while passing it through the air for a short time of 0.05s, then passed through the first stage aqueous coagulating bath for 3s, which contained 45% by weight of solvent of PVDF resin, and then through the second aqueous coagulating bath containing 10% by weight of solvent of PVDF resin for 80s. The hollow fiber-shaped extrudate thus obtained was subsequently subjected to water washing, hydrophilic agent rendering (shown in Table 2) and drying. Finally, the prepared hollow fiber membrane was taken up on the gathering wheel.

[0053] The prepared hollow fiber membrane, out-to-in, has external skin 1, complete

sponge-structure supporting layer 2 and internal skin 3 respectively, in the cross-section as shown in Figs 1, 2, 3, 4 and 5.

[0054] The microporous hollow fiber membrane had an outer and inner diameter of 1.25mm, 0.65mm respectively, an average pore diameter of 0.045 $\mu$ m, and a porosity of 78%. The compressive strength of the microporous hollow fiber membrane was 0.5Mpa, and the purity water flux per unit wall thickness was 450L/m<sup>2</sup>h (at 25°C, 1bar).

[0055] The properties of the prepared hollow fiber membrane are shown in Table 4.

## **EXAMPLE 12**

[0056] Example 1 was repeated to prepare a microporous hollow fiber membrane except for 20.5% by weight of polyvinylidene fluoride resin (1700 as trade name available from Kureha in Japan,) having a molecular weight of 500,000 daltons; 9.5% by weight of polyvinylpyrrolidone having a molecular weight of 45,000 daltons (PVP K-30 as trade name available from Shanghai Shenpu Co.); 12% by weight of PEG-400 (imported from Japan); 1.0% by weight of Tween (imported from Japan); 0.5% by weight of lithium chloride; 56.5% by weight of dimethylacetamide (available from BASF Co.).

[0057] The resulting extrudate was evaporated while passing it through the air for a short time of 0.02s, then passed through the first stage aqueous coagulating bath for 1.5s, which contained 60% by weight of solvent of PVDF resin, and then through the second aqueous coagulating bath containing 30% by weight of solvent of PVDF resin for 30s.

[0058] The prepared hollow fiber membrane has double skins which are internal and external, and a complete sponge-structure supporting layer in the cross-section.

[0059] The microporous hollow fiber membrane had an outer and inner diameter of 1.25mm, 0.65mm respectively, an average pore diameter of 0.06 $\mu$ m, and a porosity of 80%. The compressive strength of the microporous hollow fiber membrane was more than 0.5Mpa, and the water flux per unit wall thickness was 750L/m<sup>2</sup>h (at 25°C, 1 bar).

## **EXAMPLE 13**

[0060] Example 1 was repeated to prepare a microporous hollow fiber membrane except for 20.5% by weight of polyvinylidene fluoride resin (SOLEF6020 as trade name available from Solvay,) having a molecular weight of 400,000 daltons; 10.5% by weight of polyvinylpyrrolidone having a molecular weight of 45,000 daltons (PVP K-30 as trade name available from Shanghai Shenpu Co.); 10% by weight of PEG-300 (imported from Japan); 1.5% by weight of polyvinylalcohol; 5% by weight of 20% sodium acetate aqueous solution; 52.5% by

weight of dimethylacetamide (available from BASF Co.).

[0061] The resulting extrudate was evaporated while passing it through the air for a short time of 0.2s, then passed through the first stage aqueous coagulating bath for 2.0s, which contained 80% by weight of solvent of PVDF resin, and then through the second aqueous coagulating bath containing 20% by weight of solvent of PVDF resin for 4s.

[0062] The prepared hollow fiber membrane has double skins which are internal and external, and a complete sponge-structure supporting layer in the cross-section.

[0063] The microporous hollow fiber membrane had an outer and inner diameter of 1.25mm, 0.65mm respectively, an average pore diameter of 0.055 $\mu$ m, and a porosity of 80%. The compressive strength of the microporous hollow fiber membrane was more than 0.5Mpa, and the water flux per unit wall thickness was 460L/m<sup>2</sup>h (at 25°C, 1bar).

#### **EXAMPLE 14**

[0064] Example 1 was repeated to prepare a microporous hollow fiber membrane except for 19.0% by weight of polyvinylidene fluoride resin (SOLEF6030 as trade name available from Solvay,) having a molecular weight of 500,000 daltons; 9.0% by weight of polyvinylpyrrolidone having a molecular weight of 45,000 daltons (PVP K-17 as trade name available from Shanghai Shenpu Co.); 11% by weight of PEG-300 (imported from Japan); 4% by weight of polyvinyl alcohol; 2.0% by weight of Tween-80 (imported from Japan); 5% by weight of triethyl phosphate (C.P.); 50.0% by weight of dimethylacetamide (available from BASF Co.).

[0065] The resulting extrudate was evaporated while passing it through the air for a short time of 0.15s, then passed through the first stage aqueous coagulating bath for 2.5s, which containing 50% by weight of solvent of PVDF resin, and then through the second aqueous coagulating bath containing 25% by weight of solvent of PVDF resin for 120s.

[0066] The prepared hollow fiber membrane has double skins which are internal and external, and a complete sponge-structure supporting layer in the cross-section.

[0067] The microporous hollow fiber membrane of the present invention had an outer and inner diameter of 1.20mm, 0.60mm respectively, an average pore diameter of 0.015 $\mu$ m, and a porosity of 75%. The compressive strength of the microporous hollow fiber membrane was 0.5Mpa, and the water flux per unit wall thickness was 450L/m<sup>2</sup>h (at 25°C, 1bar).

Table 1: Formulation of the present invention

Component	Example									
	1	2	3	4	5	6	7	8	9	10
P/DF	Concentration (wt%)	18	20.5	19	20	25	20	22	19	23
	Characteristic Viscosity	1.95	1.75	1.75	1.8	1.65	1.85	1.68	1.87	1.65
	Molecular Weight (g/mol)	800000	500000	500000	600000	400000	650000	400000	680000	400000
	PVP(wt%)	K-30:12 K-90:0.5	K-30:9.5	K-17:9.0	K-17:12	K-17:10.0	K-30:8	K-17:12	K-30:10	K-30:8
Organic Additive	PEG(wt%)	PEG-600 8	PEG-400 12	PEG-300 11	PEG-600 12	PEG-600 12	PEG-800 10	PEG-400 10	PEG-600 10	PEG-400 5
	Polyvinyl Alcohol (wt%)			4.0		2	2			8
	Tween(wt%)	1.5		2.0			2		2.0	
	Triton (wt%)		1.0		1.0			0.5		1.0
	Lithium Chloride (wt%)		0.5				4.0	3.5		
Inorganic Additive	Lithium nitrate (wt%)	0.5							3.0	
	Sodium Acetate wt%		5.0							
	Sodium Nitrate(wt%)					1.0				0.5
	NMP(wt%)	29.5					10		50	50
Solvent	DMF(wt%)			50				50		
	DMA(wt%)	30	56.5			40	44			
	Dimethyl Sulfoxide (wt%)				55				6	
	Triethyl Phosphate (wt%)			5				2		4.5

Table 2: Hydrophilic Agent for the Present Invention

Component	Example									
	1	2	3	4	5	6	7	8	9	10
Agent	50	60	45	35	35	50	50	50	10	80
	0.1	0.1	0.1	0.1	0.2	0.1	0.3	0.1	5.0	0.05
	Hydroxypropyl Cellulose (wt%)									
	Triton (wt%)	0.5	1.0	5.0	1.0	2.0	1.0	1.0	5.0	1.0

Table 3: Lumen Forming Liquid for the Present Invention

Component	Example									
	1	2	3	4	5	6	7	8	9	10
PVDF Solvent (wt%)	50	45	40	45	42	60	80	45	50	10
Alcohol and Polyalcohol (wt%)	8	10	12	10	10	9	5	10	11	30
Surfactant (wt%)	5	0.5	1	2.0	2	0.5	0.5	2	3	5
Deionized Water (wt%)	37	44.5	47	43	46	30.5	14.5	43	36	55

Table 4: Properties of the Prepared membrane for the Present Invention

Parameter \ Example	1	2	3	4	5	6	7	8	9	10
Nominal Pore Size( $\mu\text{m}$ )	0.045	0.06	0.055	0.05	0.025	0.01	0.032	0.022	0.06	0.045
Porosity (%)	75	80	80	75	80	70	80	80	80	85
Water Flux per Unit Wall Thickness $\text{L/m}^2 \text{ h}$ (at $25^\circ\text{C}$ , 1bar)	450	750	500	450	300	150	220	350	800	600
Compressive Strength (Mpa)	0.50	0.55	0.52	0.54	0.52	0.51	0.51	0.53	0.50	0.50